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ALKENYLFLUOROCYCLOTRIPHOSPHAZENES. (U)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Several alkenylfluorocyclotriphosphazenes have been prepared and characterized. Oligomeric side products obtained in the reaction of propenyl lithium with $N_3P_3F_6$ result from anionic attack on the propenyl phosphazene. The yield of oligomers is dependent on the grade of lithium used. The mono and disubstituted vinyl ether derivatives, $N_3P_3F_6-n$ [$C(OR) = CH_2$] ($n = 1, 2$; $R = CH_3$, C_2H_5) were prepared from $N_3P_3F_6$ and the appropriate lithium reagent. Oligomeric (continued on reverse side)		

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side products are not observed. The reaction follows a geminal pathway. Reactions leading to mixed substituent derivatives, $N^3P^3F^4K[C(OC_2H_5)_2 - CH_2]$ ($X = C_6H_5, N(CH_3)_2$), have been carried out and a directive effect based on the ring substituent has been observed. Copolymerization of $N^3P^3F^4K[C(OC_2H_5)_2 - CH_2]$ with styrene has been investigated. Nmr ($^1H, ^{13}C, ^{19}F, ^{31}P$) spectroscopy studies allowed for both structural characterization and elucidation of charge distribution in the various alkenyl moieties.

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Alkenylfluorocyclotriphosphazenes

by

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University of Vermont
Department of Chemistry
Burlington, Vermont 05405

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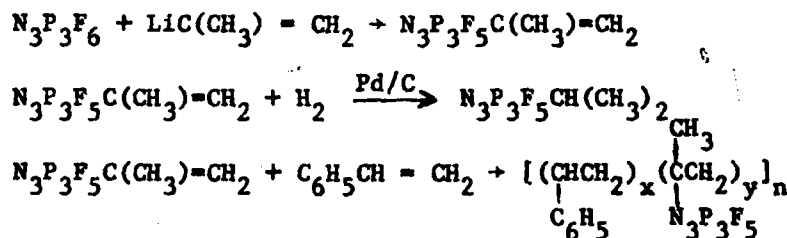
Alkenylfluorocyclotriphosphazenes

Christopher W. Allen, Randall P. Bright and
Kolikkara Ramachandran

Department of Chemistry, University of Vermont
Burlington, Vermont 05405, USA

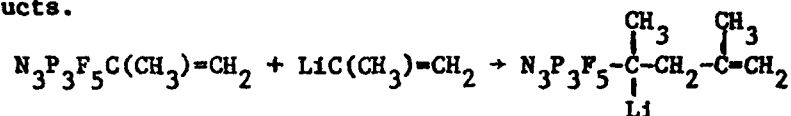
The use of organometallic reagents such as organolithium, Grignard and organocopper (1) species in substitution reactions with halocyclophosphazenes has led to the synthesis of a large number of organophosphazene derivatives (2). The vast majority of these compounds have been the aryl and alkyl derivatives. Recently, we have initiated an investigation of the synthesis, characterization and reactions of alkenylphosphazenes (3). Our interest in these materials is three-fold: comparison of the stereochemistry of substitution reactions with that observed for other organometallic reagents (2), elucidation of the electronic interaction between the phosphazene and unsaturated organic moieties (4), and synthetic transformations of the organofunctional exocyclic group (5).

We have previously reported the preparation of propenyl phosphazenes via the reactions of propenyl lithium reagents with hexafluorocyclotriphosphazene, $N_3P_3F_6$ (3). These materials undergo a broad variety of reactions ranging from simple hydrogenation (2) to copolymerization with styrene (6). Given the potential

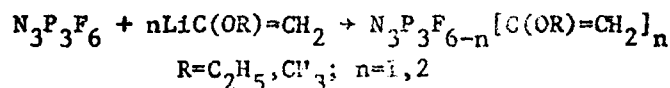


technological utility of these copolymers as flame retardant materials (6), we have now reinvestigated the reaction of 2-propenyl lithium with $N_3P_3F_6$. In addition to the expected propenylphosphazene, we obtain an oily high-boiling by-product. The ratio of propenylphosphazene to by-product is strongly dependent on the source of lithium used to prepare the organolithium reagent. The average molecular weight of a typical by-product

is around 1000 and the mass spectrum of a carefully fractionated material shows only one $N_3P_3F_5$ unit. We propose that anionic attack by the organolithium reagent on the olefinic center in the propenylphosphazene initiates the formation of the observed by-products.



Our experience with propenylphosphazenes suggested that one could avoid some of the complications in the synthesis of alkenylphosphazenes by dealing with alkenylphosphazenes containing electron donating functions on the olefin thus counteracting the electron withdrawing effect of the phosphazene. We tested this hypothesis by metalating ethylvinyl ether with tert butyl lithium and allowing the organo-lithium reagent to react with $N_3P_3F_6$. Using this reaction, we were able to prepare both the mono and disubstituted derivatives, $N_3P_3F_5C(OC_2H_5)=CH_2$ and $N_3P_3F_4[C(OC_2H_5)=CH_2]_2$, without any of the by-product observed in the case of the propenyl lithium reaction. Similar results were obtained starting with methylvinyl ether. Attempts to achieve trisubstitution led to a complex series of reactions involving

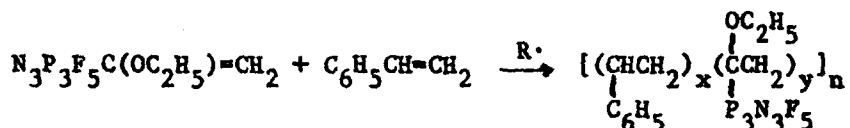


such processes as cleavage of the ethoxy group from the ethoxyvinylphosphazene. The disubstituted material was shown to have the geminal configuration (2,2- $N_3P_3F_4[C(OC_2H_5)=CH_2]_2$) by 1H , ^{13}C , ^{19}F and ^{31}P nmr spectroscopy. The monosubstituted materials show long-range fluorine coupling with exocyclic group. These interactions are not observed in the disubstituted derivatives. The ^{31}P and ^{19}F nmr spectra clearly show, by the phosphorus-fluorine coupling patterns, the presence of $\equiv PF_2$ and $\equiv PR_2$ centers and the absence of $\equiv PFR$ centers thus confirming the geminal nature of the disubstituted materials.

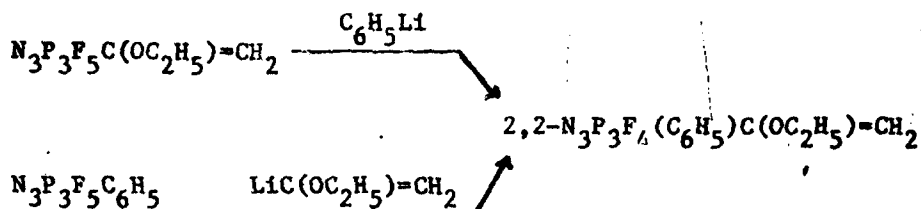
The chemical studies discussed above strongly support our hypothesis that the polarity of the organic function in alkenylphosphazenes can be significantly altered by the nature of the olefin substituents. We sought alternative methods to evaluate these effects and found that ^{13}C nmr spectroscopy is a very useful tool in this regard. Generally, the β carbon chemical shift in substituted olefins is sensitive to electronic effects at the α position (7). Thus on going from ethylvinyl ether to $N_3P_3F_5C(OC_2H_5)=CH_2$, the β carbon atom experiences a 15 ppm downfield shift and the propenyl derivative, $N_3P_3F_5C(CH_3)=CH_2$, is 32 ppm downfield from the ethoxyvinyl derivative. Similar observations hold for mixed phenyl/alkoxyvinyl and dimethylamino/alkoxy-

vinyl fluorophosphazenes. This later observation clearly shows the large difference in charge distribution in these two olefins. Examination of the ^{31}P data also has uncovered some interesting trends, for example, there is a significant difference in ^{31}P data chemical shifts when an ethoxyvinyl group is replaced by a phenyl group ($\Delta\delta = 6$ ppm). The effect of the various vinyl substituents on the ^{31}P shifts is also significant.

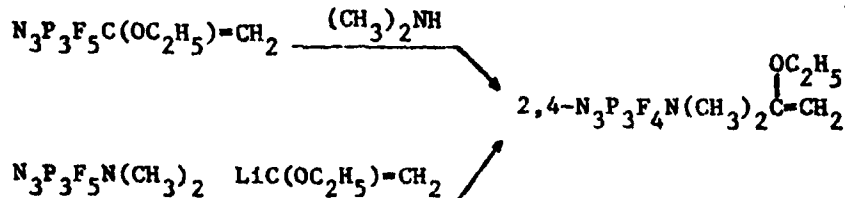
Having demonstrated that the ethoxyvinylphosphazene can be converted to the disubstituted derivative, we decided to explore a variety of reactions involving the ethoxyvinylphosphazene. Since much of our interest in alkenylphosphazenes is related to their incorporation into traditional vinyl polymers (5,6), we were pleased to observe facile copolymerization of $\text{N}_3\text{P}_3\text{F}_5\text{C}(\text{OC}_2\text{H}_5)=\text{CH}_2$ with styrene. We also have prepared some mixed substituent derivatives. The reaction of phenyl lithium with



$\text{N}_3\text{P}_3\text{F}_5\text{C}(\text{OC}_2\text{H}_5)=\text{CH}_2$ leads to the geminally substituted material $2,2\text{-N}_3\text{P}_3\text{F}_4(\text{C}_6\text{H}_5)\text{C}(\text{OC}_2\text{H}_5)=\text{CH}_2$; the same product is obtained from the reaction of ethoxyvinyl lithium with phenylpentafluorocyclo-triposphazene. However, the reaction of two molecules of phenyl lithium with $\text{N}_3\text{P}_3\text{F}_6$ is known to follow a predominantly non-geminal pathway (8).



In another series of experiments, we found that the reaction of $\text{N}_3\text{P}_3\text{F}_5\text{C}(\text{OC}_2\text{H}_5)=\text{CH}_2$ with dimethylamine leads to the non-geminal isomers, $2,4\text{-N}_3\text{P}_3\text{F}_4[\text{N}(\text{CH}_3)_2]\text{C}(\text{OC}_2\text{H}_5)=\text{CH}_2$; the same product is obtained from the reaction of ethoxyvinyl lithium with dimethylaminopentafluorocyclo-triposphazene.



The structures of all the mixed substituent derivatives were unambiguously established by ^{31}P and ^{19}F nmr spectroscopy.

The observation of the variation of the stereochemical course of the reaction of ethoxyvinyl lithium with various monosubstituted pentafluorocyclotriphosphazenes with the nature of the phosphazene substituent clearly demonstrates that there is a directive effect based on the ring substituent which is operative in these reactions. These findings are at variance with current thinking which stresses the control of the incoming reagent on the stereochemistry of the substitution reaction (9). We propose the following model for cases where substituent control of directive effects occurs. We have previously shown that exocyclic electron release in organofluorophosphazenes is through the σ system (4). The net result of this effect is that ring nitrogen atom lone pair electron density is preferentially transferred to the $\equiv\text{PF}_2$ center, thus leaving the $\equiv\text{PFR}$ center as the site of nucleophilic attack. When a π donating substituent, such as dimethylamine, is on the ring, electron release is into the phosphorus atom system at the substituted phosphorus center. This mechanism reduces the formal positive charge at the substituted phosphorus atom and hence leaves the $\equiv\text{PF}_2$ center as the site of substitution.

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